

COMPARATIVE REACTIVITIES OF PETROLEUM COKES

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INTRODUCTION

Petroleum coke is produced by coking of high boiling petroleum fractions (residua) to obtain more valuable lighter hydrocarbon products and coke. The two more prominent commercial processes for carrying out the coking operation are Fluid Coking and Delayed Coking.

Fluid Coking is a continuous process. It is carried out in equipment similar to that used extensively for Fluid Catalytic Cracking (1,2). A two vessel system is used in which the small product coke particles are heated by partial combustion in a burner vessel and these particles are circulated to the coking vessel to supply the heat needed. Finely dispersed residuum feed is injected into the coking vessel which operates at 900-975°F. The coke formed by cracking is deposited on the surface of the small coke particles which are then returned to the burner. The burner is, of course, operated at a higher temperature than the reactor. This results in some devolatilization of the coke. These volatiles along with part of the product coke (if necessary) are burned to supply heat.

In the Delayed Coking process, residuum is preheated in a furnace and is then introduced into a soaking drum. This large drum provides sufficient holding time to crack the residuum with the light hydrocarbons passing overhead. The drum eventually fills with coke which is then mechanically removed. Delayed Coking is thus a cyclic process. Coking temperatures in the drum may vary between 800 and 850°F.

In both processes the coke product represents a bottoms fraction and its chemical quality is dependent on the quality of the residuum feed. Non-volatile metals and ash constituents in the feed are deposited essentially 100% in the coke. Sulfur compounds, which are usually concentrated in the heavier petroleum fractions, are further concentrated in the coke to the extent that petroleum coke product normally contains 1.2 to 2.0 times the sulfur concentration of the residuum feed.

The volatiles content and physical properties of petroleum coke produced by Fluid Coking are quite different from the coke produced in Delayed Coking. Fluid coke is exposed to a higher temperature than is delayed coke, about 1100-1150°F. vs. 800-850°F. As a result green (i.e., uncalcined) fluid coke contains about 7 wt.% volatiles (measured at 1742°F.) vs. 10-15 wt.% volatiles in green delayed coke. Also, in Fluid Coking a layer of coke is deposited during each pass and the product has a characteristic onion ring structure, whereas delayed coke product is amorphous in nature. The differences between the two cokes are illustrated by photomicrographs in Figure 1, which

shows cross sections of particles of the two cokes.

Petroleum cokes vary in their resistance to oxidation. This is an important property of coke in many end uses. Good quality cokes, i.e., those having low metals and sulfur contents, generally are calcined and then find their way into carbon electrodes where resistance to oxidation is desirable. Low quality cokes generally are used green as a fuel and rapid oxidation is desirable.

In the work described in this paper, the reactivity of the various cokes was measured by placing the coke in a flowing stream of CO_2 at 1742°F . and recording the weight loss continuously. This technique permits close control of test conditions and does not require removal of large quantities of heat. Other investigators have studied the reaction of CO_2 with carbon. In a recent paper (3), Givry and Scalliet reported on an investigation relating anode reactivity with CO_2 to performance in an electrolytic reduction cell.

EXPERIMENTAL

MATERIALS

Samples of green fluid coke from several commercial fluid coking units were calcined in a muffle furnace to a temperature of 2400°F . The delayed cokes and the coal tar coke were from commercial production. These cokes had been calcined for use in carbon electrodes prior to receipt. Normally, a calcining temperature of about 2400°F . is used in this commercial operation.

A commercially available coal tar binder was used in the preparation of all of the molded carbon specimens. This material was obtained from the Barrett Division of Allied Chemical Company.

PHYSICAL AND CHEMICAL INSPECTIONS OF MATERIALS

Pertinent inspections of the calcined cokes used in this study are given in Table I. All tests and inspections were obtained by using techniques which are common in the carbon industry. The coal tar binder had a 215°F . softening point, a coking value of 67.5 and C/H ratio of 1.6.

REACTIVITY TEST

The reactivity of the cokes with carbon dioxide ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$) was measured in the reactivity apparatus shown in Figure 2. The sample of carbon was dried overnight at 275°F . and then was placed in the quartz tube. After heating to 1742°F . in an atmosphere of purified nitrogen, a flow of purified CO_2 was started over the sample. The CO_2 rate was about 12 liters per hour. This gave a velocity of 2.2 cm./sec. in the annulus between the sample and the quartz tube. A continuous weight recording device measured the loss of weight of the sample due to reaction with CO_2 . The inlet and exit gas rates and exit gas composition were obtained. The CO concentration in the off-gases ranged from about 3 to 30 percent varying with the reactivity of the sample.

Test data were obtained on granular coke samples and on samples of coke which had been molded into cylindrical test specimens, bound together with coal tar binder. When the reactivity of a granular coke sample was to be measured, a 16 gram sample of 14-35 mesh coke was supported in a platinum mesh basket. Reactivities of the molded carbon specimens were determined by suspending the sample on a platinum wire which passed through a small hole in the specimen. Upon completion of the test on molded specimens, the carbon body was cooled and weighed and then brushed with a stiff bristle brush. Loosely held carbon particles which could be brushed from the sample were reported as "dust." The amount of "dust" measured in this manner is related to the amount of carbon which will be lost from the carbon body as it is consumed.

PREPARATION OF THE CARBON SPECIMENS

The molded carbon specimens used in this study were prepared by mixing the coke and pitch binder in a steam jacketed sigma blade mixer. Mixing was continued for 30 minutes at 300°F. The mixture was molded to form a 3 inch diameter by 5 inch long carbon body which was then baked slowly to about 1900°F. in a muffle furnace. Reactivity test specimens about 3/4 inch in diameter by 2 inches long were cored from the baked carbon body. Three levels of binder content were used in the work reported herein and both fine grained and coarse grained carbon aggregates were employed. The fine grained aggregate consisted of about 75 wt.% 35-200 mesh coke and 25 wt.% coke ground to pass a 100 mesh screen. The coarse grained aggregate was made up of 50 wt.% 4-48 mesh coke and 50 wt.% coke ground to pass a 100 mesh screen.

RESULTS AND DISCUSSION

Comparison of Granular Coke Reactivity

Results of the study of cokes in granular form (14-35 mesh) show that fluid cokes react with CO₂ at a much lower rate than do delayed cokes. (Table I) The coal tar coke which was prepared in a manner similar to delayed coke had the highest reactivity. These data confirm results obtained by Walker et al (4) in a more detailed study of cokes. It is well known that oxidation of carbon occurs more rapidly along crystal edges than along the basal planes. Deposition of carbon in relatively thin layers on the spherical fluid coke particles results in the onion skin structure of fluid coke (5) which is shown in Figure 1. The carbon in this thin onion skin layer is probably oriented such that basal planes of the carbon structure are exposed to a greater extent than are the crystal edges. Thus, one would expect that the reactivity of fluid coke would be low. It is also possible that the higher temperature at which carbon is deposited in fluid coking results in the lower reactivity of this material compared to delayed coke.

The reactivity of petroleum coke increases with its total ash content (Figure 3). The coke was also analyzed for V, Ni, Fe, Na, Ti, Cu, Al, Cr, and Si. Among these metallic contaminants, the concentration of iron appears to correlate best with coke reactivity. It is evident that, for a given ash content, the reactivity of fluid coke is lower than that of delayed coke.

Reactivities of Baked Carbon Specimens

The reactivities of baked carbon specimens prepared from the various granular cokes are given in Table II. It is seen in Figure 4 that the rate of consumption of the carbon specimen is directly related to the reactivity of the granular cokes. This means that the bodies prepared with fluid cokes have lower consumption rates than those prepared from delayed cokes. The carbon bodies prepared with 28 wt.% binder show a higher reactivity than those prepared with 16-18 wt.% binder. This is not surprising in that the binder coke from coal tar has a higher reactivity than any of the petroleum cokes. Also, the binder coke is not baked (calcined) to as high a temperature as were the petroleum cokes and this would be expected to result in its having a higher reactivity.

The particle size distribution of the carbon aggregate does not appear to have a major influence on consumption rate of the carbon bodies. Only two comparisons of this factor were made in this study, one with delayed coke and one with fluid coke. Neither coke showed much difference in consumption rate between fine and coarse grained carbon bodies.

Most carbon bodies are consumed in commercial use either as part of the process operation or as a result of exposure to oxidizing atmospheres. When the carbon is consumed there is a tendency to form loose particles of carbon or "dust." The generally accepted explanation for "dusting" is that the binder carbon is consumed faster than the carbon aggregate. The unconsumed portion of the carbon aggregate then becomes loose and can be brushed from the main body of carbon. The amount of loose carbon formed during our experiments is shown in Table II. It is immediately obvious that the quantity of "dust" formed was much lower for the carbon bodies prepared with fluid cokes than for those prepared from delayed cokes. This is true for both fine grained and coarse grained carbon aggregates. However, the fluid coke specimens were not as reactive and less total carbon was consumed in the standard four hour test. Additional data will have to be obtained at equivalent total consumption to establish how the amount of "dusting" obtained with fluid coke aggregate compares with delayed coke at a given consumption level.

Data have been obtained which show (Figure 5) that the use of low reactivity fluid coke to supply the carbon fines reduces the formation of "dust." High reactivity delayed coke was used to supply the coarse carbon aggregate in these samples, which were made up of 50 wt.% coarse coke and 50 wt.% fine coke as described previously. For comparison, samples were prepared using delayed coke having the same particle size distribution. Both reactivity and dust formation (at the same carbon consumption) were lower for the carbon specimens containing the low reactivity fine fluid coke. One possible explanation is that the low reactivity coke fines act as a diffusion barrier and reduce the rate of consumption of the bonding carbon. Thus the overall reactivity of the carbon surface is more in balance and less dust is formed.

CONCLUSIONS

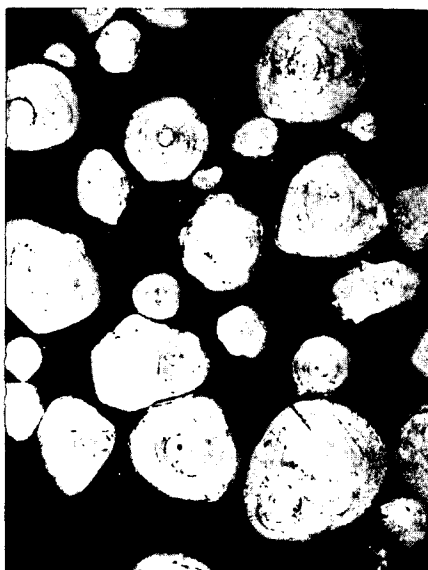
Data on nine commercially available cokes show that the process used to prepare the coke is a major factor influencing its reactivity. Ash content,

particularly iron content, is of secondary importance. Fluid coke has a lower reactivity than delayed coke at the same impurity level. The lower reactivity measured on granular cokes is carried over into carbon bodies prepared from these cokes. Binder content also influences reactivity of the carbon body. There is also an indication that less carbon dust (loose carbon) is formed when low reactivity coke is used to supply the fine coke aggregate.

LITERATURE REFERENCES

1. Voorhies, A., Jr. "Fluid Coking of Residua", Proceedings of the Fourth World Petroleum Congress, Section IIIF, Reprint 1. Rome: Carlo Colombo Publishers, 1955.
2. Voorhies, A., Jr. and Martin, H. Z. Oil Gas J. 52, No. 28, 204-7 (1953).
3. Givry, J. P. and Scalliet, R., Paper presented at the AIME Annual Meeting, February 18-22, 1962, New York, New York.
4. Walker, P. L., Jr., Rusinko, F., Jr., Rakazawski, J. F., and Liggett, L. M. "Proceedings of 1957 Conference on Carbon", 643-58. New York: Pergamon Press, 1957.
5. Dunlop, D. D., Griffin, L. I., Jr. and Moser, J. F., Jr. Chemical Engineering Progress 54, No. 8, 39-43 (1958).

FIGURE 1
COMPARISON OF UNCALCINED COKES

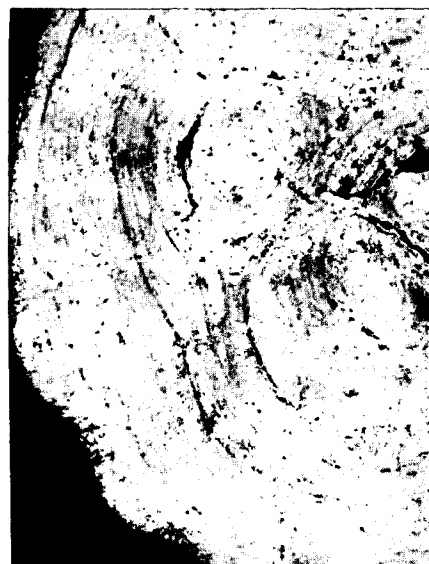


ABOUT 63X



FLUID

DELAYED



ABOUT 425X



FIGURE 2
REACTIVITY MEASURING APPARATUS

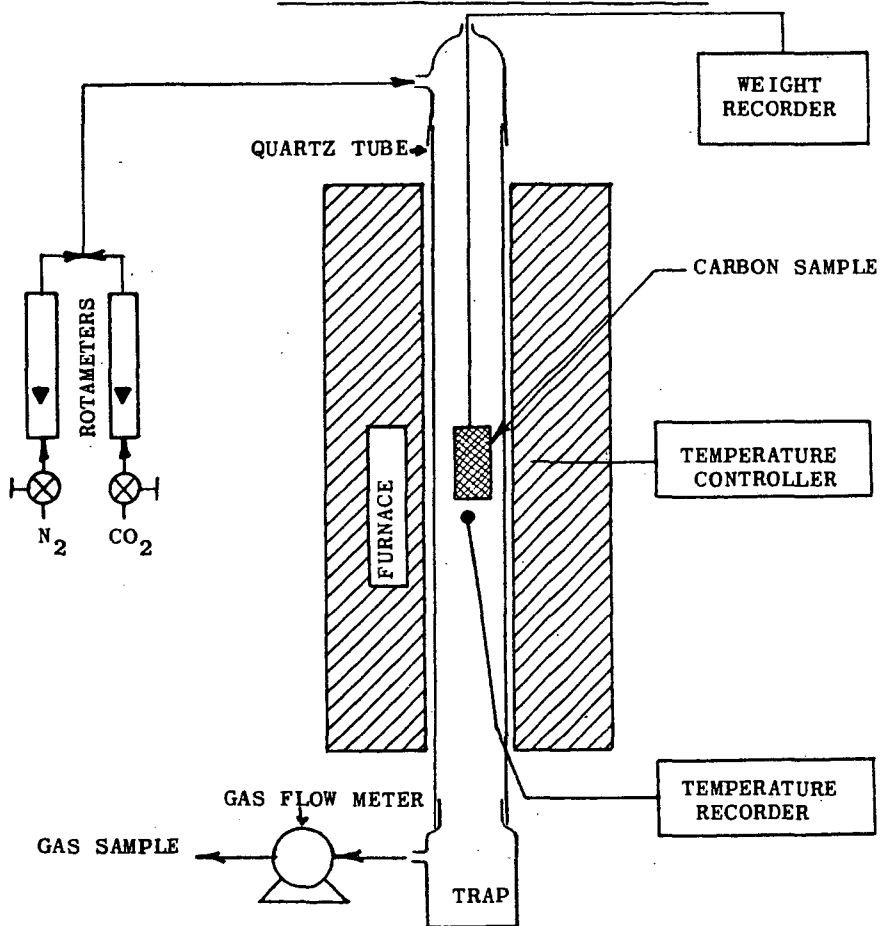


FIGURE 3
CARBON REACTIVITY IS AFFECTED BY ASH CONTENT

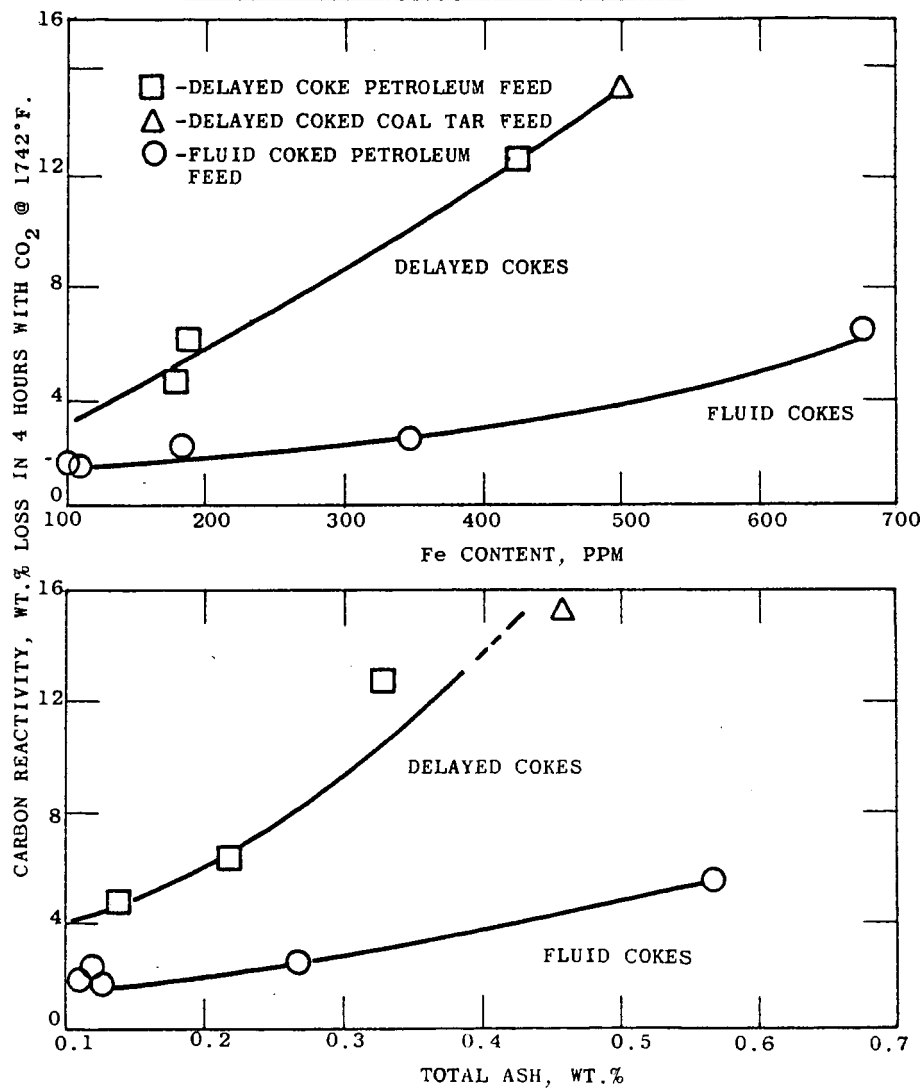


FIGURE 4
COMPARISON OF REACTIVITIES OF CARBON BODIES AND GRANULAR COKES

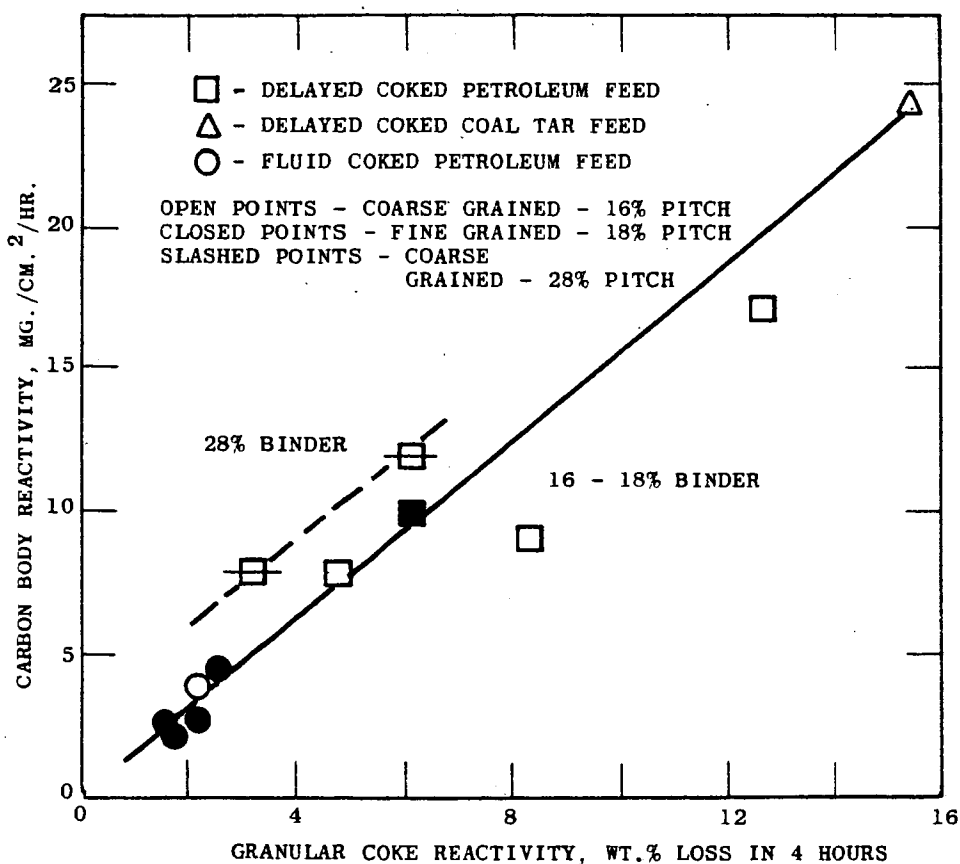


FIGURE 5

CARBON DUST FORMATION VS. CARBON CONSUMPTION IN COARSE GRAINED SPECIMENS

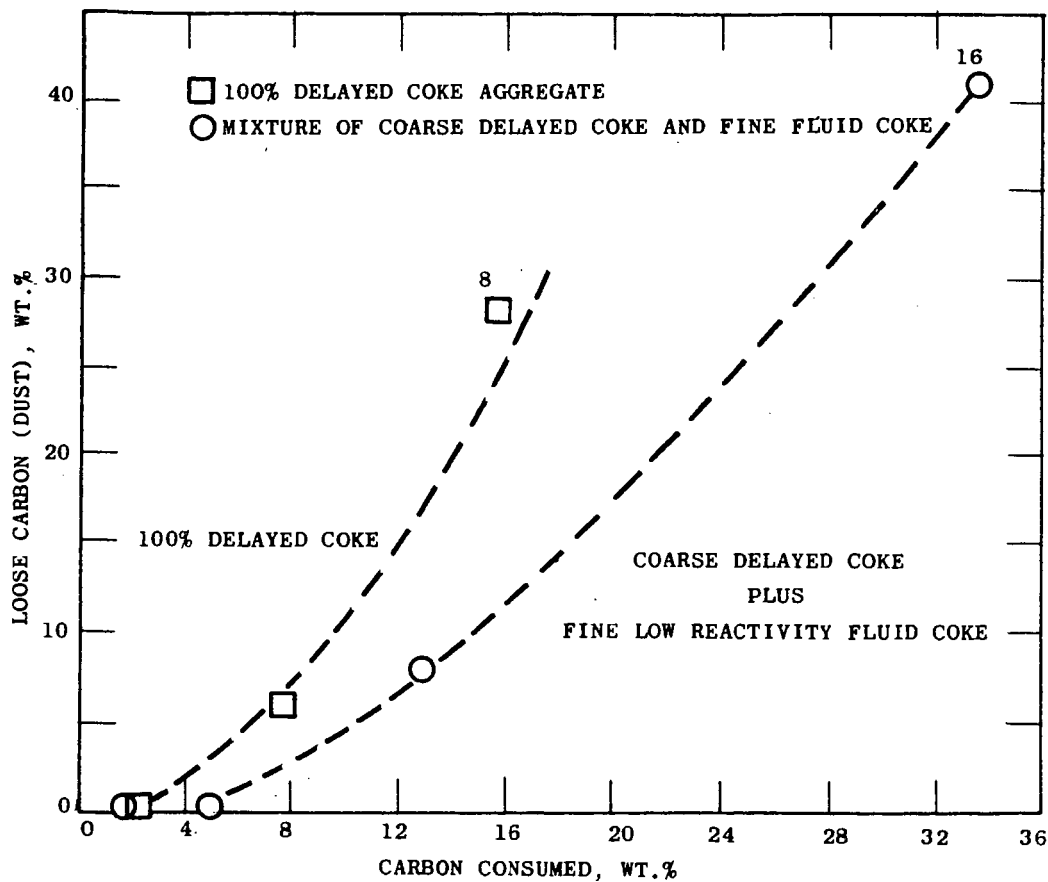


TABLE I

DATA ON GRANULAR COKES
ALL COKES WERE CALCINED AT ABOUT 2400° F.

| Sample No. | Coking Process Used | Feed Source | Impurities in Coke | | | Granular Coke Reactivity* Loss, Wt. % in 4 Hrs. |
|------------|------------------------|----------------|--------------------|---------|---------|--|
| | | | Total Ash, Wt. % | Fe, ppm | Mo, ppm | |
| DP-1 | Delayed | Petroleum | 0.14 | 180 | 125 | 4.7 |
| DP-2 | Delayed | Petroleum | 0.22 | 190 | 100 | 6.2 |
| DP-3 | Delayed | Petroleum | 0.31 | 430 | 150 | 12.7 |
| FP-1 | Fluid | Petroleum | 0.12 | 185 | 75 | 2.2 |
| FP-2 | Fluid | Petroleum | 0.11 | 100 | <50 | 1.7 |
| FP-3 | Fluid | Petroleum | 0.13 | 110 | <50 | 1.6 |
| FP-4 | Fluid | Petroleum | 0.27 | 350 | 90 | 2.5 |
| FP-5 | Fluid | Petroleum | 0.57 | 670 | 615 | 6.5 |
| DCT | Delayed | Coal Tar | 0.46 | 500 | 305 | 15.4 |

* Measured by exposing 14-35 mesh coke to CO₂ @ 1742° F. - 750C
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TABLE II

REACTIVITY OF MOULDED CARBON SPECIMENS

| Coke Aggregate | % Binder | Reactivity Test Time, Hrs. | Carbon Loss | | Loose Carbon, Wt. % |
|----------------|----------|-------------------------------|---------------------------|-------|------------------------|
| | | | mg./cm. ² /hr. | Wt. % | |
| Coarse Grained | | | | | |
| DP-1 | 16 | 4.0 | 7.9 | 5.5 | 3.2 |
| DP-2 | 16 | 4.0 | 9.7 | 6.7 | 9.2 |
| DP-3 | 16 | 4.0 | 17.0 | 11.5 | 7.8 |
| DCT | 16 | 4.0 | 24.5 | 15.4 | 11.4 |
| FP-1 | 16 | 4.0 | 4.3 | 3.0 | 0.3 |
| Fine Grain | | | | | |
| DP-1 | 18 | 4.0 | 7.9 | 5.3 | 3.4 |
| FP-1 | 18 | 4.0 | 2.9 | 1.9 | 0.2 |
| FP-2 | 18 | 4.0 | 2.2 | 1.5 | 0.3 |
| FP-3 | 18 | 4.0 | 2.5 | 1.6 | 0.2 |
| FP-4 | 18 | 4.0 | 4.7 | 3.0 | 0.3 |
| Coarse Grained | | | | | |
| DP-1 | 28 | 1.5 | 9.9 | 2.4 | 0.3 |
| DP-1 | 28 | 4.0 | 11.9 | 7.5 | 5.9 |
| DP-1 | 28 | 8.0 | 12.3 | 15.5 | 27.7 |
| DP-1 | 28 | 16.0 | 12.1 | 31.9 | ** |
| DP-1 + FP-1* | 28 | 1.5 | 7.0 | 1.8 | 0.1 |
| DP-1 + FP-1* | 28 | 4.0 | 7.8 | 5.2 | 0.5 |
| DP-1 + FP-1* | 28 | 8.0 | 9.5 | 12.7 | 7.1 |
| DP-1 + FP-1* | 28 | 16.0 | 12.4 | 33.8 | 40.9 |

* Sample FP-1 used to supply the fine coke portion.

** Unconsumed carbon disintegrated.

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